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Feasibility of diesel–biodiesel–ethanol/bioethanol blend as existing CI engine fuel: An assessment of properties, material compatibility, safety and combustion

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ABSTRACT

The global fossil fuel crisis and emission problems lead to investigations on alternative fuels. In this quest, a successful finding is the partial substitution of diesel with ethanol/bioethanol rather than completely replacing it. These blends of diesel and ethanol/bioethanol can be used in the existing CI engines without any major modifications and the most significant result of using this blend is the lower emission with almost the same performance as of diesel fuel alone. Two major drawbacks of using this blend are low miscibility of ethanol/bioethanol in diesel and low temperature instability of produced blend. However, biodiesel can be successfully added to prevent the phase separation of diesel–ethanol/bioethanol blend. Thus, this blend becomes stable even at lower temperatures and more amount of ethanol/bioethanol can be added to them. It is found that a maximum of 25% biodiesel and 5% of ethanol/bioethanol can be added to the diesel fuel effectively. Adding ethanol/bioethanol to diesel fuel alters the properties of the blend, which does not meet some of the standards. Biodiesel addition to this blend helps in regaining the fuel properties to the standard values and thus the blend can be efficiently used in the existing diesel engines. From the review, it can be said that, the use of diesel–biodiesel–ethanol/bioethanol blend can minimize the use of diesel fuel by approximately 25–30%.

Contents

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1. Introduction

The ever-increasing quest for alternative fuel has been started a few decades back. The worldwide fuel crisis of the 1970s initiated awareness about the vulnerability to oil embargoes and shortages among many countries of the world. Significant attention was then concentrated on the improvement of alternative fuel sources. When the issue of using an alternative fuel in the diesel engines comes into consideration, some important factors are needed to be considered. These factors comprise of distribution and supply, fuel delivery reliability to the engine, emissions and engine stability [1]. Besides this attention towards the alternative fuel sources, today another important concern for us is the gases causing the greenhouse effect within the earth's atmosphere and local pollution.

The most significant way to assess an automotive fuel is to judge its capability to decrease emissions, to increase the fuel efficiency and the ability to lessen the dependency on the slowly diminishing fossil oil stock [2]. Another very important factor to be considered for assessment is the difference between the modern state-of-the-art vehicles and the older technologies that represents the majority of our current vehicle fleet. Extreme environmental conditions like very cold or very hot temperatures and high elevations also play a vital role in assessing a fuel. Finally, the fuel must provide the same drivability quality as the existing conventional fuels do and the most important factor is its usability in the typical engines. The vehicle and engine technology and particularly the technology for the treatment of exhaust-gas are the factors that usually affect our decision.

The efficient use of fuels sourcing from renewable sources is an option to fulfill these challenges. Due to the availability in large volume, among all the renewable fuel sources bioethanol can be a good option especially because the second-generation production process of bioethanol is going to be available very soon in the coming years [3]. Bioethanol is produced from various feedstocks like sugarcane, corn, beet, molasses, cassava root, barley sugar, starch, cellulose, etc. In addition, ethanol can be produced from reacting ethene and steam (As this process requires a lot of energy, a major portion of the world's ethanol is produced from renewable sources through fermentation. Thus the bioethanol is mostly named as simply ethanol.). Although it is regarded primarily as a substitute fuel for SI or spark ignition engines but it also has potential uses for CI engines. During the 1980s the blending of ethanol with fossil diesel fuel was a topic of research and it was investigated that this ethanol–diesel blend, also known as diesohol, is technically usable in the then existing diesel engines without any major modifications [3]. The main advantage of ethanol is its oxygen content which is about 34% by weight [4]. Beside this oxygen content the use of ethanol with diesel fuel has many more advantages as well as some major disadvantages. Taking all these factors under consideration the usage of ethanol with diesel fuel in the diesel engines seems attractive.

The ongoing investigations and the already found analysis about the fractional replacement of fossil diesel fuel with the combination of biodiesel and ethanol in compression ignition engines found to be successful as this blend has the similar fuel properties like the commercial diesel fuel with high biofuel content. Many scientists and investigators have studied this blend with different proportions of diesel, biodiesel and ethanol to study its suitability as a fuel in the existing CI engines. Thus the aim of this review is to investigate different fuel properties of diesel–biodiesel–ethanol/bioethanol blends by varying the biofuel portions in the blends, investigated by many researchers. Finally compare the properties with the classical diesel fuel to assess its feasibility as a fuel for CI engine.

2. Diesel–biodiesel–ethanol blend as a diesel extender

The strategy of adding ethanol or bioethanol to diesel is quite complex and requires dedicated solutions. The approaches are quite multifaceted and require profound solutions. Several methodologies are identified to overcome the described issues [3].

(i) Mixing of two fuels preceding injection [5–11] i.e. injecting diesohol. The major weakness of this blend is its stability, which is very poor. It depends on the chemical composition of the diesel fuel used, the temperature at which the blend is used and the percentage of ethanol present in the blend.
(ii) Diesel fuel can be fully substituted by ethanol (approximately 95% mass): technically this solution becomes very complex, which requires major changes on the hardware of the engines to overcome ethanol's weak auto-ignition property [12]. Due to major difference in physicochemical properties between diesel and ethanol, this blend of 5% diesel and 95% ethanol becomes very difficult to use in the existing CI engines.
(iii) Fumigation of ethanol i.e. ethanol addition to the intake air charge [13,14].
(iv) Dual fuel injection; i.e. for each of the diesel and ethanol, there is a separate injection system [15].

Amongst all of the above approaches, the first one can be selected as the most feasible way to solve the baffling issues posed by others. This approach has the following benefits:

(a) No need of major technical modifications on the engine [3].
(b) Ease of operation [3].

There are some very important advantages behind considering this diesohol blend as a potential fuel for the existing CI engines. They are

(a) The diesel–ethanol/bioethanol blend can significantly reduce particulate matter (PM) emissions in the motor vehicles [2,9,16–18] (approximately 15% [19]) when compared to low sulfur diesel. Adding 10% of ethanol in the diesel fuel can reduce 30–50% of this type of emission [2].
(b) Similar energy output can be attained compared to fossil diesel fuel [20].
(c) By adding ethanol to the diesel fuel, the cold flow property is improved compared to fossil diesel fuel [4].
(d) The diesohol blends have high heat of vaporization compared to fossil diesel fuel [2].

But as suggested in some literatures [7,21–26], there are some issues which hinder the utilization of diesohol blend in the compression ignition engine.

(i) Cetane number of this blend becomes lower compared to diesel fuel. The addition of 10 v/v% of ethanol decreases cetane number by approximately 30%.
(ii) Ethanol is not completely miscible in diesel fuel. Very small proportion (less than 5 vol%) of ethanol shows complete miscibility in diesel fuel [3].
(iii) Minor variations in the fuel delivery system are required while using diesohol as fuel [8,11,27].
(iv) The density, viscosity, lubricity, energy content and the flash point of the fuel blend are affected [3]. Due to the addition of ethanol in the diesel fuel the blend's viscosity becomes lower. The addition of 10 v/v% of bioethanol decreases viscosity approximately by 10–25% [2].
(v) The swelling of T-valves fitted to Bosch-type feed pumps, which results in jammed valve stems [19].

(vi) The calorific value of the diesohol blend is much lower than the fossil diesel fuel [28].
(vii) The use of diesohol increases soot formulation [2].

To solve these problems and increase the ethanol portion in the diesohol blend an emulsifier or a surfactant can be utilized [1,9,29–34] and maintain the blend′s properties near to the fossil diesel fuel.

Different types of biodiesel can be utilized as an emulsifier or a surfactant or an amphiphile (a surface-active agent) for the long term and low temperature stability of diesohol blends [1,30,35–44]. The density of biodiesel is between 860 and 894 kg/m³ at 15 °C [45–50] and viscosity at 40 °C is between 3.3 and 5.2 mm²/s [46,47,51]. The main advantages of using biodiesel (rather than using any artificial additive synthesized in the laboratory) are as follows [52–60].

(i) The flash point of diesohol blend is very low. When biodiesel is added to diesohol then the flash point of this ternary blend becomes high enough to store it safely.
(ii) By using biodiesel, it will increase the supply of domestic renewable energy supply [54].
(iii) When biodiesel is added to the diesohol, higher viscosity and density of the biodiesel and the much lower viscosity and density of the diesohol are compensated by each other and these values come within the standard diesel fuel prescribed limits.
(iv) By adding biodiesel the heating value of the ternary blend comes nearer to the fossil diesel fuel [2].
(v) When biodiesel is added to the diesohol then the low lubricating property of diesohol blends are improved and becomes standard to use this ternary blend in the existing CI engines [20].
(vi) The high cetane number of biodiesel compensates the diesohol's low cetane number which is caused by the addition of ethanol with the diesel [2].

According to Barabás and Todorut [61] the diesel–biodiesel–ethanol blend is a great option as an alternative to diesel fuel for CI engines. The idea comes from the findings that, when biodiesel and ethanol/bioethanol are added to diesel fuel then the final fuel properties of this ternary blend becomes almost similar to diesel fuel alone except a few [2,62]. This ternary blend of diesel–biodiesel–ethanol is found to be stable even below 0 °C and have some identical or superior fuel properties to regular fossil diesel fuel [35]. Thus the addition of biodiesel in the diesel–ethanol blends or diesohol blends shows a favorable approach towards the formulation of a novel form of biofuels and fossil diesel fuel blend [4].

While conducting on-field tests Raslavicius and Bazaras [63] found positive effect on dynamic and ecological characteristics of the testing vehicle fueled with a blend of 70% of diesel + 30% of biodiesel (hereinafter – B30) admixed with the dehydrated/anhydrous ethanol additive (5 v/v%). He found no reduction of power in the diesel engine, and within the boundary of the experimental error, he found a tendency of ~2% fuel economy compared to pure B30. He found a dramatic decrease in PM (40%), HC (25%) and CO (6%) emissions compared to fossil diesel fuel while operating the vehicle at maximum power. NO_x emission from diesel–biodiesel–ethanol blends are less than (up to 4%) the B30. However, NO_x emission increases as compared to diesel fuel. Considering all these details, he concluded that a blend of 80% diesel, 15% biodiesel and 5% bioethanol is the most appropriate ratio for diesel–biodiesel–ethanol blend production, as because of the satisfactory fuel properties and reduction in emissions of the ternary blends.

3. Blend properties

Proper operation of a diesel engine depends on a number of fuel properties. When ethanol is added to the diesel fuel some of the key fuel properties are affected with specific reference to stability, density, viscosity, lubricity, energy content and cetane number of the blend. Other important factors like materials compatibility and corrosiveness are also essential to be considered [1]. To make the selection other factors like surface tension, cold filter plugging point, flash point, carbon content, hydrogen content, heating value and finally fuel biodegradability with respect to ground water contamination etc. are also needed to be considered.

3.1. Blend stability

One of the main targets of using fuel blends in the diesel engines is to keep the engine modification minimal. A solution is a single-phase liquid system, homogeneous at the molecular level. Some diesohol formulations may be a solution of ethanol/bioethanol plus additives with diesel fuel. It was seen that such blends are technically suitable to run existing diesel engines without modifications. This ethanol-blended diesel blend yielded substantial reductions in urban emissions of carbon monoxide (CO), greenhouse gases (primarily CO_2), sulfur oxides (SO_x) and particulate matter (PM). The major drawback of this diesel–ethanol blend is that, ethanol is immiscible in regular diesel fuel over a wide range of temperature. Its solubility in diesel changes with the change of ambient temperature [17,63]. Its miscibility in fossil diesel fuel is affected fundamentally by two factors, temperature and the blend′s water content. The presence of water in ethanol or diesel fuel can critically reduce solubility between the two portions [10,63]. At normal ambient temperature anhydrous/dry ethanol readily mixes with fossil diesel fuel. But below 10 °C the two fuels become separate. In many regions of the world, for a long period of time during the year this temperature limit is easily surpassed. To prevent this parting of two fuels three possible ways can be considered. They are

(i) Adding an emulsifier which performs to suspend small droplets of ethanol within the diesel fuel.
(ii) Adding a co-solvent that performs as a linking agent through molecular compatibility and bonding to yield a homogeneous blend or
(iii) Adding iso-propanol [1,9,17,29–33,64].

To stabilize the ethanol and fossil diesel fuel blend, surface active agent, i.e. an amphiphile, like Fatty Acid Methyl Ester (FAME) can also be used [1,30,35–44]. To generate a blend through the emulsification process usually heating and blending steps are required where on the other hand using co-solvents simplifies the blending method as it permits to be “splash blended”.

The solubility of ethanol in diesel fuel is affected by its aromatic content [27]. The polar nature of ethanol induces a dipole in the aromatic molecule permitting them to interact reasonably strongly, while the aromatics stay compatible with other hydrocarbons in diesel fuel. Hence, aromatics perform as bridging agents and co-solvents to some degree. If the aromatic contents of the fossil diesel fuel are compensated then it affects the miscibility of ethanol in the diesel fuel. Thus the quantity of the additive necessary to gain a stable blend, is affected [1,17,64].

Individually emulsifiers and co-solvents have been assessed with diesel–ethanol blend. Among the appropriate co-solvents, esters are used mostly because of their resemblance to diesel, which allows the use of diesel–ester blends in any proportion. The ester is used as a co-solvent, which permits the adding of more ethanol to the fuel blend. This develops the tolerance of the fuel

blend to water, and retains the blend stable, thus for a long period the blend can be stored [32,65]. The percentage of required additive is dominated by the lower limit of temperature at which the blend is needed to be stable [66]. Accordingly, diesel–ethanol blend requires fewer additives in summer conditions as compared to winter. Pure Energy Corporation (PEC) of New York was the first producer to improve an additive package that allowed ethanol to be splash blended with diesel fuel using a 2–5% dosage with 15% anhydrous ethanol and proportionately less for 10% blends [67]. PEC specified 5% additive for stability at temperatures well below −18 °C, making it suitable for winter fuel formulation. In summer, the additive requirement drops to 2.35% with spring and fall concentrations being 3.85% by volume [67]. The producer of second additive was AAE Technologies of the United Kingdom, which has been testing 7.7% and 10% diesel–ethanol blends containing 1% and 1.25% AAE proprietary additive in different states in the USA [67]. The third manufacturer was GE Betz, a division of General Electric, Inc. They produced an exclusive additive derived totally from petroleum products; compared to the earlier two, which are made from renewable resources [67,68]. This additive has been utilized in many tests, exclusively with 10% diesel–ethanol blends [67,68]. Apace Research Ltd. [19,69] of Australia, has also declared the successful improvement of an emulsification method by utilizing its pioneering emulsifier. Their diesel–ethanol blend consists of 84.5 vol% regular diesel fuel, 15 vol% hydrated ethanol (5% water) and their emulsifier 0.5 vol %. Tests were conducted by using diesohol on a truck and a bus and the results were compared with the results found using regular diesel fuel. It was investigated that larger amount of ethanol in the diesohol minimizes the regulated exhaust emissions (HC, CO, NO_x, PM) [37].

This study attempts to analyze the use of biodiesel as a potential amphiphile in this diesel–ethanol system. The study looks into the phase behavior of the diesel–biodiesel–ethanol ternary system in order to identify key areas within the phase diagram that are stable isotropic micro-emulsions that could be used as potential biofuels for compression–ignition engines. The instantaneous phase behavior indicated that the system formulates stable micro-emulsions over a large region of the phase triangle, depending on the concentrations of different components. The single-phase area of the three-component system was widest at higher biodiesel concentrations. The phase diagram indicated that at higher diesel concentrations, in order to formulate a stable micro-emulsion, the ratio of biodiesel to ethanol in the system should be greater than 1:1. The results of the study suggested that biodiesel could be effectively used as an amphiphile in a diesel–ethanol blend or the diesohol [36]. Pidol et al. [3] used a Fatty Acid Methyl Ester (FAME) to stabilize the diesel and ethanol blend. FAME stabilizes the blend by performing as a surface active agent. The investigators used Rapeseed Methyl Ester (RME) as biodiesel in this case. To raise its oxidative stability, the biodiesel was additivated with 1000 mg kg^{-1} of anti-oxidant (BHT – Butylated Hydroxytoluene). The miscibility of diesel–FAME–ethanol blend was studied broadly which lead to phase diagrams at different temperatures. As the water is harmful to the blend stability, they used an anhydrous ethanol (water content is less than 0.1%). The blends were prepared in two steps:

(1) First FAME was blended with the ethanol.
(2) Lastly, regular diesel was added to the blend.

This process was carried out as because it allows a better blend stability.

Moses et al. [70] studied micro-emulsions by using a commercial surfactant in the blend of hydrous ethanol (containing 5% water) and fossil diesel fuel. They testified that the mixtures

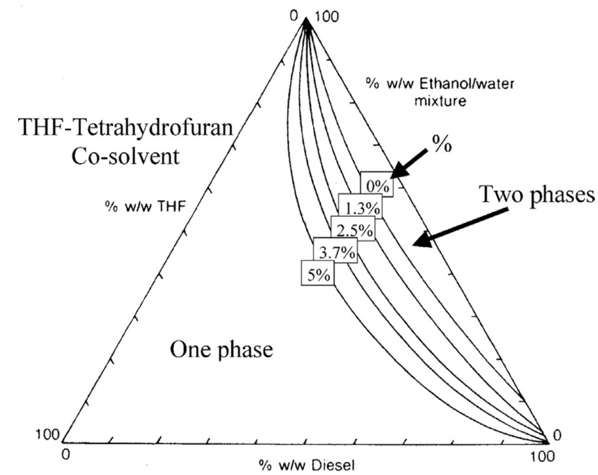


Fig. 1. Liquid–liquid ternary phase diagram for diesel fuel, tetrahydrofuran and ethanol or ethanol water mixtures with the temperature controlled at 0 °C [31].

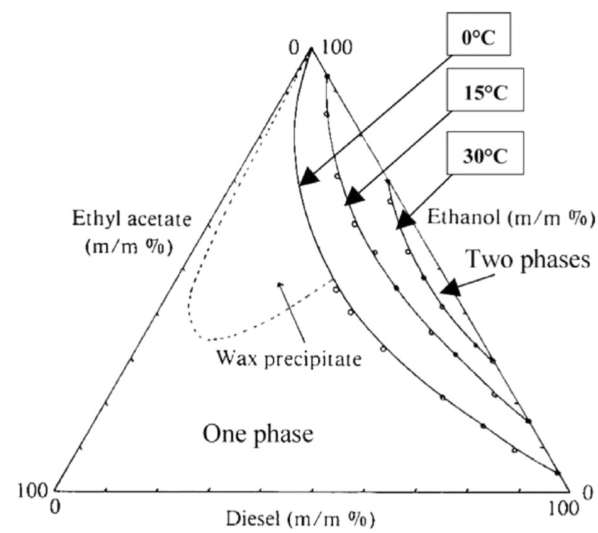


Fig. 2. Liquid–liquid ternary phase diagram for diesel fuel, ethyl acetate and dry (anhydrous) ethanol mixtures [31].

formed impulsively and negligible stirring were needed. They also appeared translucent signifying that the dispersion sizes were less than a quarter of a wavelength of light and were observed as "infinitely" stable, i.e. thermodynamically steady with no parting even after some months. According to them roughly 2% surfactant was needed for each 5% hydrous ethanol addition to the fossil diesel fuel.

Boruff et al. [71] found formulations for two micro-emulsion surfactants, one ionic and the other detergent-less. When these surfactants were applied to the diesel–ethanol (hydrous) blends then the blends were seen to be stable at low temperatures which could reach −15 °C lowest value and the blends were also seen transparent. Scientists in Sweden tried a blend of 15% hydrous ethanol (containing 5% water) with fossil diesel fuel containing DALCO, which is an emulsifying agent developed in Australia.

Letcher [66], Meiring et al. [71] and Letcher [31] found tetrahydrofuran as an effective co-solvent, which is gained at low price from agricultural waste resources. They identified another effective co-solvent, which is named as ethyl acetate. This one can also be produced cheaply from ethanol. The relative effects of the temperature and the moisture contents on the stability of the prepared fuel blends and the required amounts of co-solvents against the increasing temperature and the moisture content of the fuel blend to sustain a homogenous blend can be illustrated in

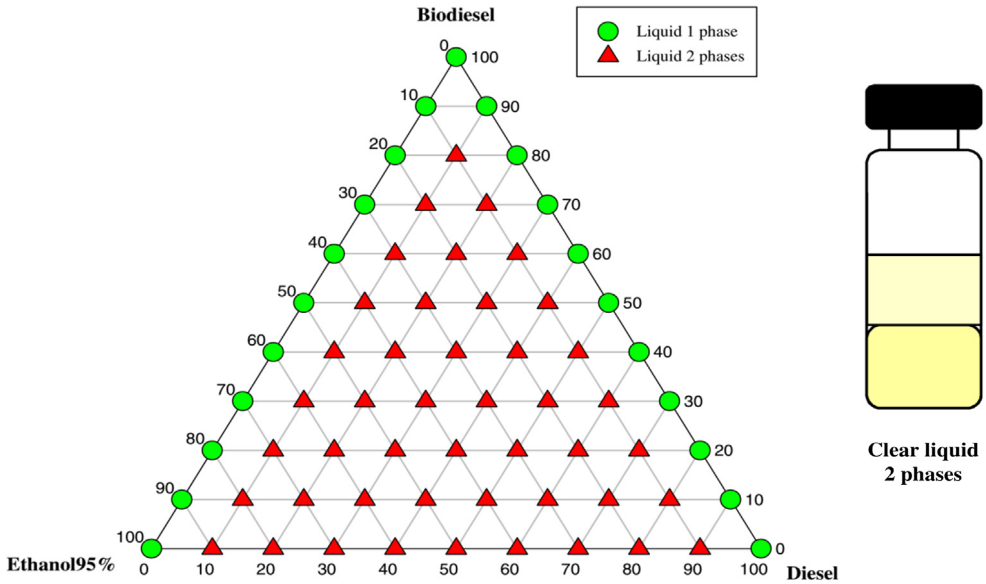


Fig. 3. Diesel–biodiesel–ethanol 95% at room temperature [37].

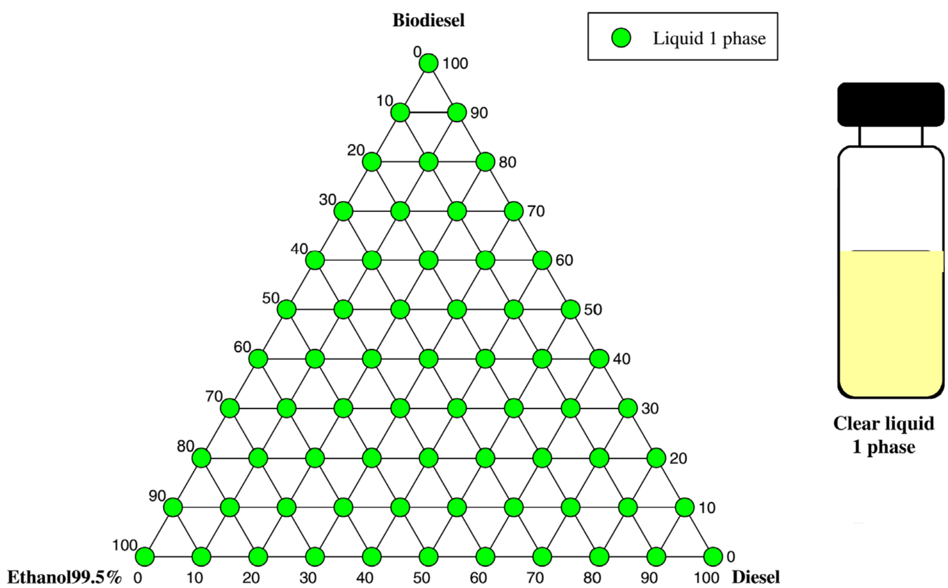


Fig. 4. Diesel–biodiesel–ethanol 99.5% at room temperature [37].

a ternary liquid–liquid phase diagram. Two such ternary liquid–liquid phase diagrams are shown below under title Figs. 1 and 2. Letcher [31] finally ended up with the conclusion that the proportion of ethyl acetate to ethanol should be consistently 1:2 to guarantee a consistent homogenous fuel blend down to 0 °C.

Rahimi et al. [41] found that the temperature of phase separation up to 4–5% bioethanol in typical diesel fuel is identical to the cloud point of the pure diesel fuel. Thus blending up to 4–5% bioethanol places no additional temperature restrictions on these fuels (if no water is present), for example, blending bioethanol with a zero aromatic diesel increased cloud point by nearly 25 °C at 5% bioethanol. Thus, it can be seen that the chemical properties of diesel fuel have a large effect on bioethanol solubility. They added sunflower methyl ester as biodiesel to increase the miscibility of bioethanol in diesel. Experimental results showed that at ambient temperature, 12% bioethanol could be dissolved in diesel. But when they increased the share of bioethanol in the blend or when the temperature decreased the observed phase separation. By adding 8% biodiesel to the blend they found increased fuel stability at low temperature close to the diesel fuel pour point without any phase separation [41].

Kwanchareon et al. [37] studied the phase stability of the ternary blend at room temperature by utilizing ethanol of three different concentrations (95%, 99.5%, and 99.9%). This was important because as the ethanol concentration affects the phase stability directly. Their findings are presented below by using ternary liquid–liquid phase diagrams of diesel, biodiesel and ethanol. The phase behavior of the diesel–biodiesel–ethanol (95%) system is presented below in Fig. 3 at room temperature.

As 95% ethanol contains 5% water, the investigators found the diesel and its blend insoluble. This happens because of the high polarity of water. This large portion of water in the ethanol enhances the polar part within an ethanol molecule. Thus diesel fuel, which is a non-polar molecule, cannot be compatible with 95% pure ethanol. Biodiesel is completely soluble in 95% ethanol in all proportions which is similar to its solubility in diesel fuel. But in this case, they found that even adding biodiesel with this diesel–ethanol (95%) blend did not increase the inter-solubility of the

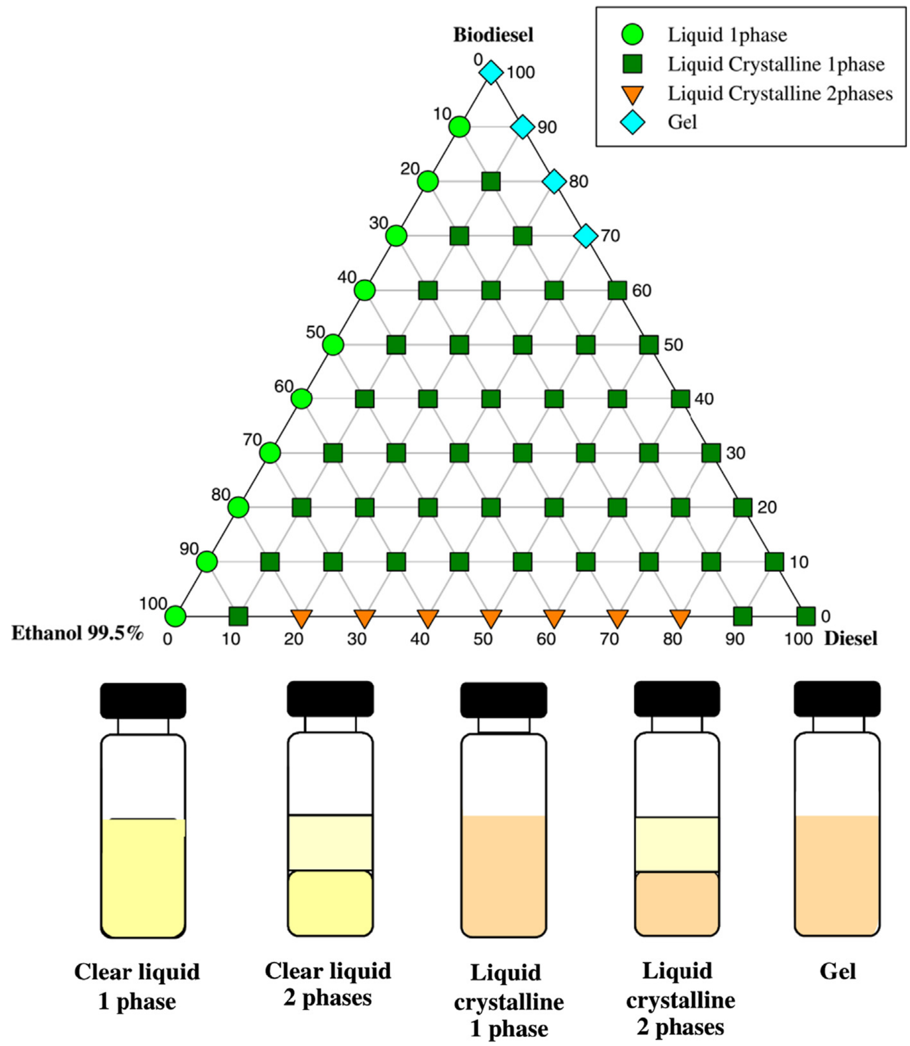


Fig. 5. Diesel–biodiesel–ethanol 99.5% at 10 °C [37].

mixture. This result of poor emulsion is due to the fact that the water in the ethanol has a stronger effect than biodiesel. Thus, it is concluded that, ethanol with higher water content is not suitable for the preparation of neither diesohol or the ternary blend of diesel–biodiesel–ethanol. On the other hand, when ethanol is used of 99.5% purity then the inter-solubility of the three liquids is not limited. These three could be used to prepare a uniform solution at any proportion as shown in Fig. 4 below.

This ethanol of 99.5% purity is more soluble in diesel fuel than the ethanol of 95% purity because of later ones low water content. Despite having low water content they found that some blends of 99.5% ethanol and diesel were being separated into phases but the blends those contained biodiesel as an additive to the blends were still one phase liquid. This homogeneity while using biodiesel can be explained by the fact that the biodiesel turns into an amphiphile (a surface-active agent) when added to the diesel–ethanol blend and forms micelles which have polar heads and non-polar tails. These molecules are attracted to the liquid/liquid interfacial films and to each other. These micelles can act in an either way, polar or non-polar solutes. This action of biodiesel depends on the orientation of its molecules. When the diesel fuel is in the continuous phase, the polar head in a biodiesel molecule concerns itself to the ethanol while the non-polar tail concerns itself to the diesel. Depending on the physical parameters and component proportions this phenomenon holds the micelles in a thermodynamically stable state [36]. The results obtained by testing ethanol of 99.9% purity are seen to be the same as the results found for 99.5% ethanol. It was seen that ethanol of 99.9% purity could also be used to prepare a homogeneous liquid solution at any proportion [37]. They also observed the phase stability at different temperatures. In Fig. 5 below, they found that at 10 °C ethanol in the range of 20–80% by volume and diesel fuel blend is a clear liquid and in crystalline phases. Biodiesel and ethanol mix to form a real solution, which can easily be prepared. Blends comprising of 70–100% biodiesel without ethanol in the blend becomes a gel. This is probably due to the presence of fatty acid in the biodiesel component.

In Fig. 6, it is seen that at 20 °C nearly all the blends are 1 phase liquid except for the blends having ethanol from 30% to 70% with diesel. In these proportions of ethanol the mixtures are always in 2 phases in which the two components are completely immiscible with each other. Thus at 20 °C, if the diesel fuel concentration is lower than 30% or greater than 70%, then the ethanol is fully miscible in diesel fuel. When the room temperature was 30 °C/ 40 °C they found all the blends as a single phase liquid. At these temperatures, ethanol could be blended with diesel at any proportions. Thus, there is no problem of phase separation at 30 °C and up to 40 °C. These results prove that diesel–biodiesel–ethanol blends can remain stable as a single phase liquid fuel at relatively high ambient temperatures (30–40 °C) [37].

Guarieiro et al. [72] also studied the phase stability of both binary (diesohol) and ternary (diesel–biodiesel–ethanol) blends at

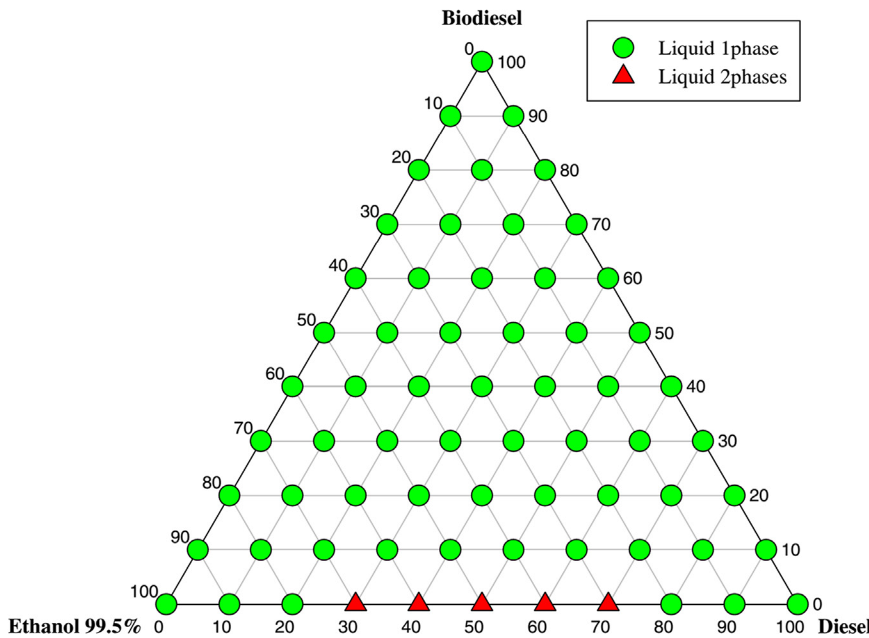


Fig. 6. Diesel–biodiesel–ethanol 99.5% at 20 °C [37].

room temperature with varying ethanol concentrations. They studied the effects of both anhydrous ethanol (99.5%) and hydrous ethanol (95%). They also found that hydrous ethanol (95%) was insoluble in diesel, as because hydrated ethanol contains 5% water which means that the co-solvents investigated, did not develop the inter-solubility of the ethanol (95%) and diesel blend. On the other hand when they added 10% anhydrous ethanol (99.5%) in the diesel fuel, they found no phase separation even after 90 days of scrutiny. But they observed that adding a greater percentage of anhydrous ethanol (15%) to the binary mixture (only diesel & ethanol/diesohol) causes phase separation on the first day. So they prepared blends using a higher percentage of anhydrous ethanol, diesel fuel and soybean biodiesel (SB), castor biodiesel (AB), residual biodiesel (RB), soybean oil (SO) and castor oil (AO) as co-solvents (at a time) and observed the stability of the ternary blends. They found some of the blends stable even after 3 months of observation while most of them were separated into phases. They described the homogeneity due to act of the co-solvents (the biodiesel and vegetable oils) they used, which act as an amphiphile (a surface-active agent) and form micelles which consists of polar heads and non-polar tails which is similar to the previous description.

Thus the investigators selected some binary and ternary blends for further study as they were stable for a 90 day period. They selected the following blend ratios [72]:

(a) Diesel/ethanol – 90/10% (DE),
(b) Diesel/ethanol/SB – 80/15/5% (DESB),
(c) Diesel/ethanol/AB – 80/15/5% (DEAB),
(d) Diesel/ethanol/RB – 80/15/5% (DERB),
(e) Diesel/ethanol/SO – 90/7/3% (DESO),
(f) Diesel/ethanol/AO – 90/7/3% (DEAO).

Cheenkachorn et al. [20] also tested several diesohol blends with different compositions of diesel and ethanol to study the homogeneity of the blends and the consequence of the emulsifiers used. Their fuel blends were little different from the others as they used hydrous and anhydrous ethanol together in most of the blends. They used palm oil biodiesel and 2-octanol as emulsifiers. They found that the solubility of diesohol blends rises as the quantity of 2-octanol and biodiesel increases. They also found that, greater amount of hydrous ethanol (which also contained some portion of anhydrous ethanol) in the blend obliges higher quantity of emulsifiers to stabilize the emulsions. These results agree with the earlier findings. The structural affinity between various component mixtures can be reinforced by the amphiphilic structures of the biodiesel and the 2-octanol at the diesel/ethanol–water interface [7]. The hydrocarbon tails or oleophilic group in the biodiesel has a strong attraction with diesel fuel while the polar head or the carboxyl group represents the hydrophilic portion, which is oriented towards the ethanol–water interface [73]. The investigators also found that, if the portion of ethanol (if both hydrous and anhydrous ethanol is used together in the blend) exceeds approximately 6.4% in the diesohol blend then even biodiesel cannot prevent the blend from phase separation. In addition to this, they summarize the use of 2-octanol in a manner that, its proper amount can lead to the lesser possibility of water separation from the blends. They also mentioned that in order to balance the hydrophilic and hydrophobic portions of the blend, the amount of 2-octanol should be high enough. They concluded that, for the blends containing ethanol (if both hydrous and anhydrous ethanol is used together in the blend) higher than 6.6% will need a minimum amount of 4.3% 2-octanol to avoid the phase separation. And when the percentage of ethanol (if both hydrous and anhydrous ethanol is used together in the blend) is less than 0.8% of the blend then the biodiesel can perform properly [20].

3.2. Density

Density is a very important property of any fuel which affects the engine performance characteristics directly [74]. Other properties like cetane number and heating value are also associated within density. Fuel atomization efficiency and combustion characteristics are influenced by its density [74,75]. The injection system used for diesel fuel, measures the fuel by volume thus the variation of the fuel density will affect the output power of the engine due to an altered mass of injected fuel. Generally higher density causes greater fuel flow resistance which results in higher viscosity which may lead to inferior fuel injection. Density of ethanol is inferior to diesel fuel density where the density of biodiesel is higher than the diesel.

Barabas et al. [76] tested density of several diesel–biodiesel–ethanol blends and found that the density of these ternary blends are very close to the diesel fuel density on the entire considered temperature domain (0–80 °C) [76].

Park et al. [77] tested the elementary properties of diesel–biodiesel–bioethanol (bioethanol portion in every ternary blends were kept fixed which was 20%) blends as the biodiesel portion in the blends was increased gradually. They conducted all their experiments at a blend temperature of 15 °C. They found that the blend density which drops with the accumulation of bioethanol in the blend [76,78,79] again escalates with the biodiesel addition. Thus the spray momentum is recovered. Specifically a blend containing 60% diesel, 20% biodiesel and 20% bioethanol is denser than that of fossil diesel fuel [80].

Kwanchareon et al. [37] prepared some ternary blends with different diesel, biodiesel and ethanol ratios for fuel property testing. They also found that the density of the blends decreases as the percentage of ethanol increases in the blends which is attributed to the fact that ethanol has a low density which lowers the final density of the blends. Again when the percentage of biodiesel is increased in the blends, the final density of the blends increases due to the density of the biodiesel, which is greater than the former two components. However, they found density values of all the blend satisfactory and within the acceptable limits for the standard diesel engines. These outcomes match the same trend as those of earlier works [28,37,72,81,82].

3.3. Calorific value

Heat of combustion or the calorific value of a fuel blend is another very important property to determine its suitability as an alternative to diesel fuel. Lower heating value or the net calorific value of a fuel blend influences the power output of an engine directly. The calorific value of both the biodiesel and the ethanol/bioethanol is less than the diesel fuel. Thus their addition to the diesel fuel lowers the calorific value of the final blend lower than the diesel fuel. As the amount of biofuel (biodiesel and ethanol) is increased in the ternary blends, the calorific value of the final blends decreases [35,43,82–86]. This is the result of the lower calorific value of ethanol and biodiesel. However, the blends containing ethanol, lower than 10% are seemed to have a heating value nearer to fossil diesel fuel [37]. Calorific values of different ternary blends, investigated by many investigators and scientists are tabulated at the end of the review.

3.4. Viscosity and lubricity

Viscosity is another very important fuel property. It affects the fuel drop size, the jet penetration, quality of atomization, spray characteristics and the combustion quality [74]. The operations of the injection systems in the CI engines are also affected by it, especially at lower temperatures, when the fluidity of the fluid is reduced [76]. For every engine there is a highest and a lowest limit for the viscosity of a fuel to be used in that engine. If very low viscous fuel is used, it could cause the fuel system leakage. It typically results in smaller sauter mean droplet diameters, thereby increasing the surface area of the fuel droplets and significantly influences the evaporation characteristic time [87,88]. On the other hand high viscosity of the fuel can cause the followings:

(1) Poor fuel atomization and incomplete combustion.
(2) Increasing the engine deposits.
(3) Requiring more energy to pump the fuel.
(4) And causing more problems in cold weather as because the viscosity increases as the temperature decreases, i.e. the fluidity of the fuel is reduced at low temperature conditions.

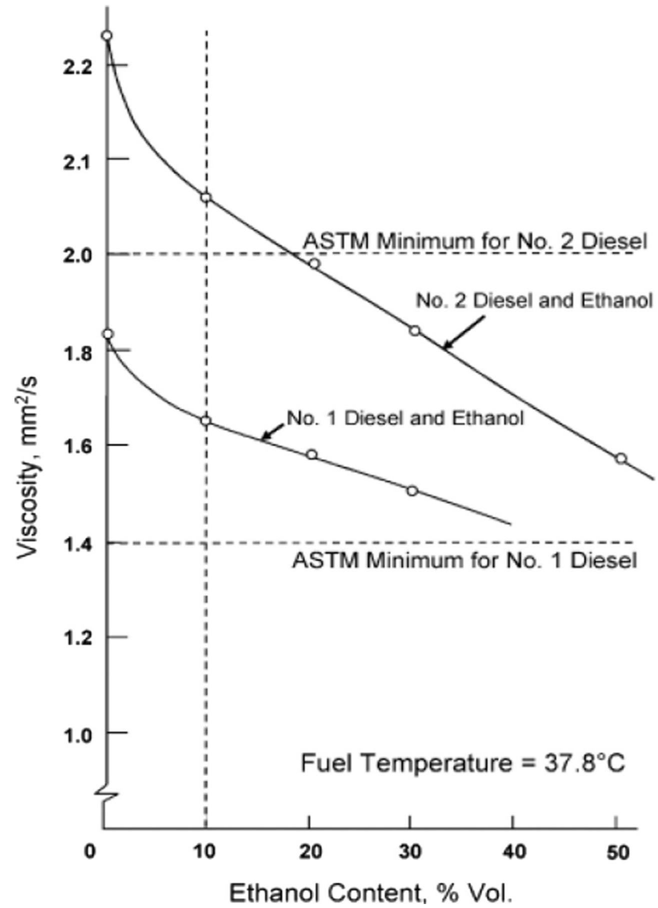


Fig. 7. Effect of ethanol content on fuel blend viscosity [89].

Thus it should be low enough to flow freely at its lowest functioning temperature. Fuel pump lubrication & injectors are also affected by the fuel viscosity [74], especially those incorporated with rotary distributor injection pumps which rely completely on the fuel for lubrication within the high pressure pumping mechanism. In the case of the common rail accumulator fuel-injection system, the fuel delivered to the rail by the high pressure pump also depends on the fuel for lubrication. There is less dependence on the fuel for lubrication in the case of in-line pumps and unit injectors; but still there are few metal interfaces like the interface between the plunger and barrel require lubrication by the fuel. Injector lubrication, particularly at the needle guide-nozzle body interface is also affected [1]. It is eminent to mention that the viscosity of the final blend depends on the diesel fuel viscosity. To ensure the durability of the fuel injection system and the reliability of starting the engine when it is hot, minimum viscosity and lubricity of the fuel blends are mandatory [1]. When ethanol is blended with diesel fuel, which has got a viscosity nearer to the minimum (approximately 1.10 mm^2/s at 40 °C), yields an overall viscosity of the blend lower than the ASTM minimum. This decreased viscosity of the diesohol blends significantly affects the fuel injection system's lubrication. Again when biodiesel is added to this blend, its high lubricity compensates the low lubricity of the diesohol blends. A friction modifier can also be added to the blend to prevent such troubles [3].

Wrage and Goering [89] created the graph shown in Fig. 7 below by studying the deviation of kinematic viscosity with the amount of ethanol present in the blend.

Barabás et al. [76] prepared several blends with different portions of diesel, biodiesel and ethanol. They found that the

viscosity value of the blends is very near to the fossil diesel fuel and as the temperature increases the differences with diesel fuel gets lesser. This is due to the fact that the temperature of vaporization of ethanol is pretty small (approximately 78 °C). It vaporizes at the operating injector temperatures [76].

Park et al. [80] found that, kinematic viscosity significantly increases when biodiesel fuel is added to the diesel–ethanol blend. They kept the portion of bioethanol in the diesohol blends fixed (20% by volume) and added biodiesel in an incremental way to study its effect on the viscosity of the final blends. From Fig. 8 below, it is seen that, as the biodiesel content in the diesohol blends increases, the kinematic viscosity also increases. Viscosity mostly rises with the chain length of the fatty acid in a fatty ester, and biodiesel fuel comprises of fatty ester and fatty acid [90].

Zöldy [2] measured the viscosity according to EN ISO 3104:1994. He prepared several ternary blends for viscosity measurements. His results also show that, when ethanol and biodiesel are added to diesel fuel then the final viscosity of the fuel blends comes nearer to the fossil diesel fuel. He has perceived the underneath formula in the field of 30–60 °C for determining the viscosity of a ternary blend containing diesel, biodiesel and ethanol/bioethanol.

$$\eta_{kev} = (2n_e\eta_e + 3n_{bd}\eta_{bd} + n_g\eta_g + 0.71)0.91$$

where η_{kev} is the viscosity of the blend; n_i is the ratio of components (e – ethanol, bd –biodiesel, g – diesel); η_i is the viscosity of components (e – ethanol, bd – biodiesel, g–diesel).

The author concluded from the experimental results that, from the point of view of utility, a joint blend of ethanol and biodiesel has a low decreasing effect on blend viscosity. The author suggested that the blends can be used as diesel engine fuel due to their viscosity parameters [2].

3.5. Surface tension

Regarding the droplet formation and combustion of fuel, an important parameter need to be considered is the fuel's surface tension [91,92]. It is difficult to form droplets of fuel (liquid) with a high surface tension [92]. As the content of biodiesel increases in the ternary blends, the surface tension of the blends increases linearly [77], and as the ethanol content increases in the blends, the surface tension decreases [61]. Barabas and Todorut [61] found the variation in the surface tension of the ternary blends in the range of $-1,8\ldots+20.1\%$. Their ternary blends contained 5–25% biodiesel and 5–10% ethanol [61].

3.6. Fuel oxygen content

The use of oxygenated fuel improves fuel combustion and reduces the engine emission level. Several oxygenated compounds were used for this purpose but the most common ones are biodiesel, alcohols and ethers. Ethers that are octane enhancers increase fuel oxygen content but their use is limited because of the cancer risk probability and non-renewability. On the other hand, bioethanol and cellulosic ethanol are aliphatic alcohols which are produced from plants and agricultural wastes and are more suitable in comparison to the other alcohols. Fig. 9 below shows the effect of fuel oxygen content on HC and CO emissions. This figure shows that 2% total mass of oxygen is more suitable because of the peak HC reduction [41].

Ribeiro et al. [32] and Shi et al. [65] found that the addition of esters to the ethanol–diesel blends increases the oxygen level in the blends.

Rahimi et al. [41] studied the prepared blends for determining oxygen content. They found the oxygen content of bioethanol, diesel and biodiesel as 34%, 0.0% and 11.01% respectively. The oxygen content of diesel–biodiesel–bioethanol blends were calculated from the following relation:

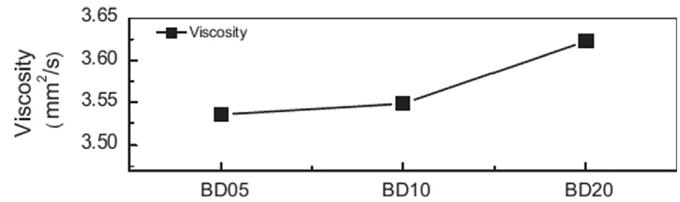


Fig. 8. Diesel fuel viscosity results for the increase of biodiesel in diesel–bioethanol blends. The fuel temperature is 15 °C [80].

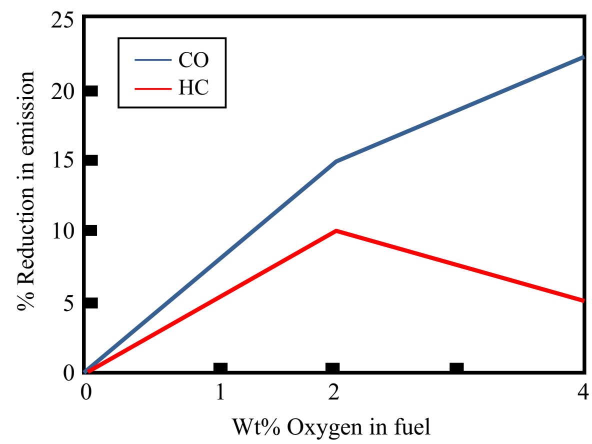


Fig. 9. Effect of fuel oxygen content on HC and CO emissions [41].

$$M_o = 0.34\rho_e V_e + 11\rho_b V_b$$

where M_o is the mass of oxygen in blends (g); ρ_e is the density of bioethanol (g/cm^3); ρ_b is the density of biodiesel (g/cm^3); V_e is the volume of bioethanol in the blends (cc); and V_b is the volume of biodiesel in the blends (cc) [41].

For increasing the oxygen by a certain amount in the diesel fuel, the amount of biodiesel and ethanol could be varied in different proportions. For instance, for adding 10 g oxygen to 1 kg fuel, several proportions could be available. It is possible to add 30 cc bioethanol and 20 cc biodiesel to 950 cc diesel. Another selection is to add about 25 cc bioethanol and 40 cc biodiesel to 935 cc diesel. In the first selection, it is necessary to add 50 cc oxygenated compounds (30 cc bioethanol+20 cc biodiesel) to 950 cc diesel fuel but in the second selection this amount increases to 65 cc. It means that the bioethanol plays a major role in increasing the fuel oxygen content [41].

3.7. Flash point

Flash point and flammability limits of a fuel describe its flammability. Flammability limits can be described as the maximum and minimum concentrations of combustible vapor in the air and the temperatures at which the vapor occurs, that will propagate a flame after sufficient ignition energy is provided. The flash point is the temperature of the lowest value, which is corrected to a barometric pressure of 101.3 kPa at which the vapor overhead the sample is ignited with the application of an ignition source under specified test conditions. It gives an estimation of the temperature at which the vapor pressure reaches the lower flammable limit. It does not affect the combustion directly rather high flash point of fuel makes it safer regarding its handling, transportation and storage [93]. The flash point of biodiesel should be greater than 120 °C (EN 14214), for fossil diesel, it should be

higher than 55 °C (EN 590) and in the case of bioethanol it should be below 16 °C [62].

While handling and storage of an alternative fuel comes into consideration (using existing facilities), then the most important property of the fuel which is needed to be considered is its flammability limits. During refueling or when damage or leaks occur in any fuel system components, then flammable conditions might occur in the partially filled fuel tanks. This condition is the result of the vapor produced through the evaporation of the fuel.

At ambient temperature fossil diesel fuel generates inadequate vapor to reach its lower flammability limit. On the occasion of gasoline, the upper flammability limit is exceeded by the vapor concentration. With a flash point of approximately 13 °C, ethanol falls between the gasoline and fossil diesel fuel in terms of flammability temperature limits and flash point. Thus ethanol/bioethanol can produce ignitable vapor at normal ambient temperature above the fuel level. The flash point of many diesel–ethanol blends or diesohol blends were measured and found that whatever the ethanol ratio was, the two fuel mixture characteristically reaches to a flash point value (measured between 12 and 15 °C) which is close to the value of pure ethanol [3]. And in the case of diesel–biodiesel blends, the flash point increases as the biodiesel content in the blends increases [75]. Thus this concerns the fire safety issue.

Prommes Kwanchareon et al. found the flash point of diesohol blends (diesel–ethanol blend) very low, within the range of 12–17 °C [37]. When biodiesel is added to this blend, the flash point of this blend (biodiesel–diesel–ethanol) is mainly lead by ethanol.

Barabás et al. [76] found that all the blends having ethanol had high flammability with a flash point that is lower than the ambient temperature. This institutes an important disadvantage regarding their transportation, distribution and storage. Thus precautions are needed to be taken in handling and transporting the fuel. Thus special and proper ways of management are required for storage, handling and transportation of these diesel–biodiesel–ethanol blends to avoid explosions.

Prommes Kwanchareon et al. also found all the ethanol containing blends with a high flammability and a flash point temperature which was less than the ambient temperature, thus affecting the shipping and storage classifications. They also mentioned that the flash point of the diesohol blends is dominated by the portion of the fuel in the blend which has the lowest flash point among the other blend components. Thus the storage, handling and transportation of diesohol blends require special attention compared to fossil diesel. These findings are similar to the other discussed above [10,28,35,37,81]. At standard ambient temperatures in closed vessels like storage tanks, the flammability characteristics of the diesel–ethanol blends are more or less like those of ethanol in a closed vessel thus possessing a potential threat of generating ignitable vapor above the fuel level inside the tank. As a result, there is a risk of fire or explosion which has to be managed very carefully.

Due to the low flash point of ethanol, the flash point of the ternary blends also becomes very low. Barabas and Todorut [61] found the flash point of the ternary blends to be in the range of 16–18 °C, which contains up to 5% ethanol. But the blends, which contain more than 5% ethanol have a flash point less than 16 °C [41,61].

Main benefits and disadvantages of several liquid hydrocarbons were studied and it was found the iso-pentane (C5) as the most suitable one. Certainly, it is obtainable from the refinery, it is non-toxic and it exhibits a low flash point (< -51 °C) which permits reducing the incorporation proportion (7 vol% in this study). Due to this iso-pentane the flash point decreases below -17 °C, which ensures the neighboring gaseous phase to be too rich to flare up when open to a possible ignition source [3].

Thus it is seen that the flash point of the diesel–biodiesel–ethanol blends is dominated by the ethanol portion of the blends; whatever the type of biodiesel is used. The flash point of these ternary blends is such, that it could be classified as a Class I liquid and should be handled safely while filling a fuel tank and has to use the same infrastructures as the gasoline [43].

3.8. Cold filter plugging point (CFPP)

The trouble-free flow of a fuel at the lowest temperature in a particular fuel system can be estimated by the fuel's Cold Filter Plugging Point (CFPP). It is a requirement for the fuel which is a climate-dependent (between -20 °C and 5 °C temperate climate) [62]. The CFPP of biodiesel depends on the raw materials used to produce it [61].

Barabás et al. [76] observed that Cold Filter Plugging Point decreases in the case of blends containing 5% ethanol, but it has got a higher value for the blends containing 10% ethanol, which is due to the limited miscibility. This limits its usage at lower temperatures.

3.9. Cetane number

Cetane number (CN) of a CI engine fuel can be defined as the measurement of the combustion quality of a fuel during compression ignition. The cetane number and cetane index is in proportion to the density value [76]. The measurements those determine the overall fuel quality, cetane number (CN) is a significant one among them. The requirements of a minimum cetane number depend on the engine design, size, nature of speed, and load variations, as well as starting and atmospheric conditions. Using fuels of cetane number higher than the requirement does not materially increase the performance of the engine. Accordingly, to ensure maximum fuel availability the specified cetane number should be up to a certain limit. Again using fuels with low cetane number than the actual requirements could cause rough operation of the engine. Problem like difficult starting, especially in the cold weather or at high altitudes are faced by using this type of fuels. Formation of lube oil sludge is also accelerated by using this type of fuel. Besides several low cetane number fuels are the cause of larger engine deposits which results in extra smoke than usual, increased exhaust emissions and greater engine wear. Based on the cetane number of the constituents and the mass composition of the blend, the cetane number of that specific blend is assessed [62,94]. The lower cetane number means longer ignition delays, allowing more time for the fuel to vaporize before combustion starts. Initial burn rates are higher causing more heat release at constant volume, which is a more efficient conversion process of heat to work. Nevertheless it is preferable to add an ignition improver to raise the cetane number of diesel–ethanol blends so that they fall within an acceptable range equivalent to that expected of No. 2 diesel fuel [1].

As specified by the ASTM Standard D 975-02 the minimum cetane number for No. 2 diesel should be 40. Typically, the cetane number for No. 2 diesel fuels vary from 45 to 50. With the opposite relationship of cetane number and octane number, ethanol displays a low cetane rating. Hence as the ethanol concentrations in the diesel increases, the cetane number of the blend decreases proportionately [1]. The lesser the cetane number the shoddier will be the ignition property. Engine performance, its start-up and the combustion control are affected by the cetane number of the fuel being used [76]. The ester, which has a large cetane number, added to the blend offsets the reduced cetane number, which happened due to the addition of ethanol. Thus the engine ignition is improved [32,65].

Hardenberg and Ehnert [95] stated that, describing the ignition characteristics of diesohol blends based on the cetane number is unreliable. They showed the reason of discrepancy in determining the cetane numbers lower than 30. However they projected the cetane number of ethanol in between 5 and 15.

Schaefer and Hardenberg [77] assessed some ignition improvers giving special importance to the biomass-derived nitrates for ethanol fuel. They found a substantial dependency of the energy release per equivalent nitrate on the molecular weight of the ignition improving nitrate.

Hardenberg and Schaefer [96] found triethylene glycol dinitrate (TEGDN) as the most suitable ignition improver in tests performed in Brazil, particularly since it could be produced from ethanol.

Meiring et al. [97] found the ignition delay of a 30% diesel–ethanol blend as same as the diesel fuel by adding 4.5% octyl nitrate ignition improver.

Barabas et al. [76] found that, due to the very low cetane number of the ethanol, the cetane number of the diesel–biodiesel–ethanol blend decreases. However, due to the high cetane number, biodiesel can recuperate this property, thus the fuel blend can achieve the cetane number requirement for diesel which is 51 CN [98,99].

Pidol et al. [3] found that the blend containing 20% of ethanol, 40% RME and 40% fossil diesel fuel, presents a poor auto-ignition property compared to European standards with a cetane number of 44.5. When higher cetane number Fischer–Tropsch (FT), is replaced by the fossil diesel fuel then the resulting cetane number of the fuel blend becomes 54.9 which fits the EN590 specifications. The FT base fuel has got a high auto-ignition property which balances the poor one containing ethanol very well. As the cetane number is very poor of the iso-pentane; which is less than 30 [100], a lower cetane number was anticipated of the fuel blend containing iso-pentane. But this fuel blend exhibited an unpredicted higher value of 55.4. This result could be described by the high volatility of the iso-pentane, inside the CFR engine which might vaporize before the measurement. So, two fuel blends, having the identical cetane number could represent different ignitability due to the presence of iso-pentane [3].

Rahimi et al. found through their experiments that the cetane number of bioethanol was extremely low (5–8) compared to the diesel fuel cetane number (47). Using 12% bioethanol to the diesel fuel reduces fuel blend cetane number to 40. But adding sunflower methyl ester to the blend the cetane number improves due to the higher cetane number of sunflower methyl ester (54) in the present case. This cetane number could be regarded as a suitable one to be used in diesel engines [41].

Kwanchareon et al. [37] found decreasing of cetane number of the diesohol blend with the increasing amount of ethanol in the blend, which was due to the low cetane number of ethanol which is roughly 5–8. They also reported the same results as the previous study. They found that the sample comprising of 80% diesel, 15% biodiesel and 5% ethanol has a maximum cetane number which they measured to be 48.66 [37].

Zöldy [2] studied different ternary blends for measuring cetane number. The investigators here also concluded that, there is a decrease in the cetane number of the blend with the addition of ethanol and increase again with the addition of biodiesel, which matches the other described results above. They developed a multi-linear model, which can be applied for modeling the compensation factor of adding ethanol and biodiesel to diesel fuel. The model rose to be the like as displayed below for the dependency of cetane numbers on the amount of ethanol and biodiesel. The attained formula [2] shows the dependency on the components:

$$CN_{ebdg} = CN_d - 0.59n_e + 0.55n_{bd}$$

where CN_{ebdg} is the calculated cetane number of the blend; CN_d is the cetane number of diesel oil; n_e is ethanol ratio in the blend [v/v%]; n_{bd} is biodiesel ratio in the blend [v/v%].

Due to the ethanol addition a decrease of 0.6 in cetane number is well-compensated by adding biodiesel, which again increases the cetane number by an amount of 0.55. They suggested that if it is desired to hold the cetane number of the blend at its original value even after adding ethanol and biodiesel then these two components should be blended approximately at a 1:1 ratio with the diesel fuel [2].

Park et al. [80] concluded that, increasing the biodiesel amount in the blend increases the blend cetane number as the biodiesel fuel has a greater cetane number compared to both diesel fuel and ethanol. Normally, the cetane number of the used biodiesel is associated with the varieties of feedstocks used in its making. In addition, the long fatty acid carbon chains and more saturated molecules results in a high cetane number [101,102].

3.10. Pour point

The pour point is the lowest temperature at which a liquid can flow. As the temperature of a fuel approaches to its pour point it becomes cloudy due to the formation of crystals and finally the crystals solidify. This causes major operability problems [103].

Kwanchareon et al. [37] prepared many blends for testing. They found that the sample blends containing 85% diesel and 15% biodiesel, 90% diesel and 10% biodiesel have the identical pour point at 3 °C while the other samples containing only biodiesel and diesel without ethanol had the pour point which is identical to the diesel fuel. The reason behind this similarity is that, biodiesel generally has a pour point higher than conventional diesel while the ethanol has a very low pour point. But as the diesel was the main component of the ternary blends they did not find much deviation in the pour point from the fossil diesel fuel pour point value.

Due to the extremely low pour point of ethanol, its addition to the diesel fuel decreases the pour point of the final blend significantly. This is a major advantage of using ethanol in the ternary blends. Although biodiesel has high pour point (max 12 °C) than diesel and ethanol, it does not affect the pour point of the final blend [43,82].

4. Materials compatibility issue

The use of ethanol in the gasoline engines caused several material compatibility studies during the early 80s. Several of these studies are also valid for studying the effect of using diesel–ethanol blends in the diesel engines and especially in the fuel injection system [1]. The quality of the ethanol has a strong influence on its corrosive effects [96]. In addressing the problems of ethanol corrosion, Brink et al. [104] divided ethanol corrosion into three categories: general corrosion, dry corrosion and wet corrosion. General corrosion was caused by ionic impurities, mainly chloride ions and acetic acid. Dry corrosion was attributed to the ethanol molecule and its polarity. De la Harpe [105] reviewed reports of dry corrosion of metals by ethanol and found that magnesium, lead and aluminum were susceptible to chemical attack by dry ethanol.

Wet corrosion is caused by azeotropic water, which oxidizes most metals [104]. Freshly formulated blends containing pH neutral dry ethanol would be expected to have relatively little corrosive effect. However, if a blend has been standing in a tank for sufficient time to allow the ethanol to absorb moisture from the atmosphere, it may tend to be more corrosive as it passes through the fuel injection system [105]. In addition, the fuel may stand in

the fuel injection pump for a number of months, for example in a combine harvester engine, thus allowing the fuel time to corrode parts of the pump internally. Corrosion inhibitors have been incorporated in some additive packages used in ethanol diesel blends [105].

Non-metallic components have been affected by ethanol with particular reference to elastomeric components such as seals and O-rings in the fuel injection system. These seals tend to swell and stiffen. Resin-bonded or resin-sealed components also are susceptible to swelling and seals may be compromised [106].

5. Safety and biodegradability

The flammability of alternative fuels during handling and storage is of particular concern when considering their introduction into existing facilities. The vapor produced by the evaporation of motor fuels can create a flammable condition in partially filled fuel tanks during refueling, and when damage or leakage occurs in tanks or other fuel system components [107]. In the fuel tank headspace, rising temperatures will produce fuel vapors, which progress from a too-lean-to-burn, to combustible, to too-rich-to-burn [108].

Battelle [109] provided a comparison for neat diesel fuel, ethanol and gasoline, which showed that ethanol fell between diesel fuel and gasoline in terms of flashpoint and flammability and temperature limits. However, both the minimum and maximum concentration limits were higher than those of diesel fuel and gasoline. He concluded that 10–20% ethanol and No. 2 diesel fuel blends have similar flashpoints (approximately 12 °C) and upper flammability limit temperatures (42 °C), thus making the fire-safety independent of the quantity of ethanol in the blend. He also found the flammability characteristics of diesel–ethanol blends more similar to ethanol than diesel fuel with flammable vapors (above the liquid level) within storage tanks at roughly 12–42 °C compared to diesel fuel at 64–150 °C. Temperature in the fuel tank of the diesel fueled vehicles is raised approximately to 93 °C due to the recirculation of the fuel. This recirculation of fuel is essential for the cooling of the fuel injection system.

An important disadvantage of high flammability is the ignition of the plume of vapor leaving the tank while refueling the tank. This might cause due to static discharge, external sparks or smoking materials [107]. Another source of ignition is the electric fuel pumps used in the fuel tank. It has been found that the usual amount of energy in a spark initiated by a break in the inductive circuit at the current levels of these pumps is sufficiently strong to ignite a flammable mixture [107].

Speidel and Ahmed [110] assessed some alternative fuels for their biodegradability characteristics which includes a blend with diesel fuel, 15% ethanol and 5% PEC additive. They found this blend to be 70% more biodegradable than the usual diesel fuel. They also tested this blend for long term stability under the sunlight and heat exposure. They found diesel fuel to form a dark irreversible residue under such conditions, while on the side the color of the blend deepened but no residual matter was detected [111].

6. Combustion characteristics

Hulwan et al. [4] found increase in ignition delay at low loads due to the high latent heat of evaporation of ethanol and the low cetane number of the ternary blends. The investigators performed experiments where the combustion processes were similar for the test fuels. These experiments consist of a step of premixed combustion which is followed by a step of diffusion combustion. They also found the premixed combustion to be delayed, and the highest heat release rate increases for the blends. For this performance they suggested the rise of total ignition delay as responsible. Due to having lower viscosity and density, ethanol leads to superior fuel mixing and atomization to form an air fuel mixture that burns more rapidly and thus releasing more heat in the stage of premixed combustion. Due to the increased blending ratio of ethanol, the fuels in the blend with the low density and surface tension were well mixed with the air. This was because of the evaporation of ethanol droplets. This behavior points out that the macroscopic spray performance and atomization performance are both improved [78]. They found the ethanol in the blend slightly affects the spray cone angle and spray tip penetration, whereas the size of droplets of diesel–ethanol fuel blend decreases with an upsurge in the ethanol blending ratio. Although the commencement of the heat release is delayed for blends, the conclusion of heat release remains at nearly the equal crank angle as that for diesel. This indicates the decrease of diffusive combustion for blends, which might be the result of improved mixing, atomization and access availability of oxygen (inbuilt in fuel blend) [112,113]. From the rate of heat release analysis they concluded in higher thermal power output [4]. They also noticed variations in the combustion characteristics of the blends with respect to speed. Due to the availability of sufficient time for combustion, a durable premixed burning phase resulted and gives growth to the peak cylinder pressure which is near the TDC at low engine load of 1200 rpm. On the other hand the entire combustion process is shifted in the expansion stroke by the increased ignition delay which is caused at low load of 1600 rpm. As the portion of ethanol in the blend increases this propensity of the blend also increases as well. They found that especially in the blends with high ethanol content, the initialization of combustion is delayed compared to diesel fuel. This consequence indicates that the impact of a low cetane number of the blends is reduced on the ignition delay at high engine load.

Kannan [85] tested a ternary blend (50% D, 40% BD and 10% E) at 6.2 bar BMEP (Brake Mean Effective Pressure) condition. The investigator found maximum cylinder gas pressure of 74.5 bar at 366.5° CA at 25.5° BTDC (Bottom Top Dead Center) and when the injection pressure was 240 bars, which was 1.5% higher than the diesel fuel. This high pressure is due to the ethanol present in the blend which helped in producing more combustible mixture within the ignition delay period [114,115]. In the case of heat release rate variation at 6.2 bar BMEP condition, he found highest heat release rate of 27.8 J/°CA at 240 bar injection pressure and injection timing of 25.5° BTDC. He also investigated the variation of ignition delay for the ternary blends at different injection timings and pressures. He found the ignition delay of the ternary blends decreasing with the increasing BMEP. Overall the blends showed a higher ignition delay compared to diesel fuel irrespective of injection timing and pressure.

Park et al. [80] compared D100 (100% diesel) and BD05 (blend containing 5% biodiesel) and found the extension of ignition delay caused by the blended bioethanol (which was kept at 20% in all the ternary blends) in diesel fuel due to the reduction in cetane number [116–118]. In addition to this, this extension in the ignition delay is the cause of the consumption reaction of the hydroxyl radical (–OH), which confines the heat release [119]. In assessment of the B05, B10 and B20, the ignition delay is found to be shorter in length as the quantity of biodiesel fuel increases. This indicates that the start of ignition advances as the biodiesel portion in the blend increases. They found progress of the spray in the piston bowl in the event of 5° BTDC and 15° BTDC and they located the spray at the squish and crevice regions in the event of 30° BTDC in the test engine [120,121]. In addition to these, the blends containing 5%, 10% and 20% biodiesel are found to have relatively wide spray shape in the combustion chamber which is the effect of

Table 1
A comparative study of stability and physicochemical properties of diesel-biodiesel-ethanol/bioethanol blends with different biofuel portions at different temperatures.

D:BD:EtoH	Miscibility and stability of blends	Density kg/m^{3-} [4,20,26,38,43,62,76,85]	CFPP °C [62]	Viscosity mm^2/s [4,20,26,38,43,62,85]	Lubricity µm [62]	Surface tension mN/m [62]	Flash point °C [4,43,62,85]	Cloud Point °C [85]	Calorific value kJ/kg [4,20,26,38,43,62,85]	Cetane number [4,20,26,43,62,85]	Pour point °C [4,43,85]	Carbon content % by weight [4,20,26,62]	Oxygen content % by weight [4,26,38,62]
70:10:20 JBD 99.7%	–	832.87[a]	–	2.380[c]	–	–	14	–	39,930	50	−3	78.69	7.77
50:20:30 JBD 99.7%	–	834.55[a]	–	2.401[c]	–	–	12.5	–	38,965	50	−9	74.49	12.12
50:10:40 JBD 99.7%	–	820.42[a]	–	2.018[c]	–	–	12	–	36,338	41	−12	72.07	14.53
85:12:3 SBD 99.7%	3 months at NAC	840[b]	–	3.01[c]	–	–	–	–	41,500	–	–	–	2.3
80:16:4 SBD 99.7%	3 months at NAC	840[b]	–	3.03[c]	–	–	–	–	41,200	–	–	–	3.1
75:20:5 SBD	–	845[b]	–	3.04[b]	–	–	–	–	40,900	45		83	3.9
60:30:10 WCOBD 99.9%	1 month at 30 °C	826[d]	–	2.44[d]	–	–	18.5	−1	39,100	47.3	−3	–	–
50:40:10 WCOBD 99.9%	1 month at 30 °C	831[d]	–	2.60[d]	–	–	19	3	38,700	47.2	−3	–	–
50:30:20 WCOBD 99.9%	1 month at 30 °C	821[d]	–	2.14[d]	–	–	15	4	37,850	47.2	−6	–	–
90:5:5 RSOBD 99.3%	30 h at 20 and 0 °C separated in 2 phases after 30 h at −8 °C	843.7[a]	−18	2.435[c]	305	30.79[b]	17.5	–	41,707	51.04	–	83.22	2.20
85:10:5RSOBD 99.3%	30 h at 20 and 0 °C 30 h at Separated in 2 phases after 30 h at -8 °C	845[a]	−17	2.421[c]	232	34.62[b]	14	–	41,560	51.20	–	82.79	2.76
80:15:5 RSOBD 99.3%	30 h at 20 and 0 °C Clear with sediments after 30 h at −8 °C	847.2[a]	−13	2.527[c]	276	34.66[b]	16	–	41,414	51.36	–	82.37	3.32
75:20:5 RSOBD 99.3%	30 h at 20 and 0 °C Clear with sediments after 30 h at −8 °C	849.6[a]	−17	2.645[c]	243	32.86[b]	17	–	41,269	51.52	–	81.94	3.88
70:25:5 RSOBD 99.3%	30 h at 20 & 0 °C Homogeneous and clear after 30 h at −8 °C	851.9[a]	−16	2.756[c]	252	34.83[b]	18	–	41,124	51.68	–	81.52	4.43
75:15:10 RSOBD 99.3%	30 h at20 and 0 °C Clear with sediments after 30 h at −8 °C	844.7[a]	−4	2.374[c]	272	30.66[b]	15.5	–	40,668	49.24	–	80.80	4.96
70:20:10 RSOBD 99.3%	30 h at 20 and 0 °C Clear with sediments after 30 h at −8 °C	846.8[a]	−7	2.480[c]	264	31.77[b]	16	–	40,524	49.41	–	80.38	5.52
80:15:5 POBD (PME) 99.5%	1 phase liquid after 3 months at room temperatures	838.3[a]	–	2.63[c]	–	–	17	–	43,800	53.2	3	–	–
80:15:5 POBD(PEE) 99.5%	1 phase liquid after 3 months at room temperatures	837.8[a]	–	2.72[c]	–	–	15.7	–	39,300	–	3	–	–
80:15:5 POBD(PBE) 99.5%	1 phase liquid after 3 months at room temperatures	837[a]	–	2.73[c]	–	–	15	–	43,700	–	3	–	–
85:10:5 POBD (PME) 99.5%	1 phase liquid after 3 months at room temperatures	836.1[a]	–	2.57[c]	–	–	15	–	43,700	52	3	–	–
85:10:5 POBD(PEE) 99.5%	1 phase liquid after 3 months @ room temperatures	835.9[a]	–	2.63[c]	–	–	15	–	43,900	–	3	–	–

Table 1 (*continued*)

D:BD:EtoH	Miscibility and stability of blends	Density kg/m^3– [4,20,26,38,43,62,76,85]	CFPP °C [62]	Viscosity mm^2/s [4,20,26,38,43,62,85]	Lubricity µm [62]	Surface tension mN/m [62]	Flash point °C [4,43,62,85]	Cloud Point °C [85]	Calorific value kJ/kg [4,20,26,38,43,62,85]	Cetane number [4,20,26,43,62,85]	Pour point °C [4,43,85]	Carbon content % by weight [4,20,26,62]	Oxygen content % by weight [4,26,38,62]
85:10:5 POBD(PBE) 99.5%	1 phase liquid after 3 months at room temperatures	835.4^a	–	2.65^c	–	–	16	–	44,000	–	3	–	–
82.5:12.5:4.5:0.5 (HE) POBD 99.5%	Homogenous blend after 3 months at room temperature	829^a	–	2.82^c	–	–	–	–	44,430	56.20	–	–	–
84:11:4.75:0.25 (HE) POBD 99.5%	Homogenous blend after 3 months at room temperature	828^a	–	2.69^c	–	–	–	–	44,560	57.91	–	–	–
82.5:12.5:4.75:0.25 (HE) POBD 99.5%	Homogenous blend after 3 months at room temperature	829^a	–	2.78^c	–	–	–	–	44,490	57.60	–	–	–
80:15:4.5:0.5(HE) POBD 99.5%	Homogenous blend after 3 months at room temperature	830^a	–	2.97^c	–	–	–	–	44,210	56.32	–	–	–

D Diesel; BD Biodiesel; EtoH Ethanol/bioethanol; NAC Normal Ambient Condition; JBD Jatropha Seed Biodiesel; SBD Soybean Biodiesel; WCOBD Waste Cooking Oil Biodiesel; RSOBD Rapeseed Oil Biodiesel; POBD Palm Oil Biodiesel; PME Palm Oil Methyl Ester; PEE Palm oil Ethyl Ester; PBE Palm oil Butyl Ester; RME Rapeseed Oil Methyl Ester; HE Hydrous Ethanol.

[a] at 15 °C.
[b] at 20 °C.
[c] at 40 °C.
[d] at 27 °C.

active evaporation of bioethanol. This affects the higher peak combustion pressure in the blended fuels compared to conventional diesel fuel. On the other hand, a small advance in the premixed combustion phasing (CA50) (Crank Angle at 50%) is observed due to the increase of biodiesel portion in the blend, and it has a slight effect on the premixed combustion period (CA50–CA10).

This combustion phenomenon can be described in the following steps. The relatively undersized ignition delay caused by the escalation of biodiesel portion makes the premixed duration decrease. But, again the increased amount of biodiesel content results in the upsurge of the oxygen content and the cetane number; therefore, it ended in a better mixture formation. Thus, the premixed combustion length indicated almost alike values, irrespective of the biodiesel contents. On the other hand, the ignition delay for all test fuels considerably increased when the injection timing advances. In addition to this the rise of biodiesel content in the blends caused the decrease of the IMEP (Indicated Mean Effective Pressure). It can be explained by the following reasons: the premixed combustion phasing and the advancement of ignition timing, the increase of negative work before the Top Dead Center (TDC), the reduction of LHV (Lower Heating Value) and the low combustion pressure in the expansion stroke. The investigators calculated the heat release by using the law of thermodynamics from the curve of combustion pressure. They showed that the event of heat release marginally advances based on the growth of biodiesel portion. The highest rate of heat release for the blends did not show a clear tendency according to the accumulation of biodiesel fuel, but it was either similar to or higher than that of diesel fuel. This is the result of the extended ignition delay and the rise of premixed mixture [80] (Table 1).

7. Conclusions

Fulfilling the requirements to meet the diesel standard is an important part while formulating the alternative fuel blends. Biofuel blends could help us with the decreasing fossil fuel deposit and lowering engine emission. Some investigators investigated the comparison of diesel–biodiesel–ethanol/bioethanol ternary fuel blends properties to the fossil diesel fuel, whereas others tried to find out their stability. Some of them studied the conventional diesel combustion whereas others tried other approaches to use it successfully as a replacement for diesel fuel. It is technically impossible to use diesohol in the CI engine due to its physical properties, which does not meet the diesel fuel standard and this dissimilarity from the diesel fuel does not compromise the operational integrity of an engine turned to run on fossil diesel fuel. After all these works review, it can be said that it was a success, as none of them found much difficulty using this ternary fuel blend in the CI engine. The following conclusion can be made from this review which will help us to focus on the matter preciously.

(1) Phase separation occurs within the blend at low temperatures but researchers had found additive to this blend whose use can keep it stable even at −15 °C.
(2) The density of diesel–biodiesel–ethanol blends is located near the maximum limit of the specified value of EN 590.
(3) The kinematic viscosity values and the lubricity values are within the standard limits.
(4) Some of the investigators found this blend more suitable for cold climates compared to diesel fuel (this characteristic needs more investigations to be confirmed).
(5) The sulfur content of this ternary blend is less than the diesel fuel as oxygenated compound is added to the diesel fuel, which can be increased by adding more oxygenated compound.

(6) This blend shows better properties of water tolerance than the diesel–biodiesel or the diesel–ethanol blends.
(7) The heating value of this ternary blend decreases as the amount of ethanol increases.
(8) The cetane number of this ternary blend is acceptable and it is near to the diesel one.
(9) Some investigators reported unstable and incomplete combustion at lower loads (this needs more investigation).
(10) This ternary blend helps to replace maximum 25–30% of diesel with biofuel (biodiesel & ethanol), which helps in saving approximately 30% diesel worldwide.
(11) The disadvantage of this blend is found to be not safe for storage and transport but this property can be developed by adding additive like iso-pentane, which ensures its safety and transport.

These discussions indicate that from the point of view of fuel properties (e.g. flash point, pour point, cetane number, viscosity, density, safety) with a small fuel consumption penalty (which is equal to the decrease of energy content), this blend can be suggested for especially medium and small load engines. Maximum of 20–25% biodiesel and 5% ethanol can be added effectively and efficiently with the fossil diesel fuel. However, there is a scope of research on suitable additive which would increase the ethanol and biodiesel portion in this ternary blend.

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